Charge traps and emission kinetics in LuAP:Ce

J. Glodo* and A. J. Wojtowicz

Institute of Physics, N. Copernicus University, Grudziądzka 5/7, PL 87-100 Toruń, Poland

ABSTRACT

In this contribution we demonstrate the influence of shallow charge traps on emission kinetics of $LuAlO_3:Ce^{3+}$ (LuAP:Ce) scintillator. Shallow traps through their interference with the recombination process not only introduce into the emission time profiles long components (afterglow) but also can change the rising and decaying parts of time profiles. The lifetime of excited Ce^{3+} ion in LuAP crystal is ~18 ns, while the excitation at 78 nm leads to the emission described by 21.5 and 1.22 ns decay and rise time constants, respectively. Furthermore, temperature dependence of time profile shapes is observed. The analysis of emission kinetics measured against temperature shows that observed features can be explained in terms of a trap described by the following parameters: E = 0.142 eV and $s = 6.087 \times 10^{10}\ s^{-1}$.

Keywords: recombination, traps, emission kinetics, scintillators, phosphors, LuAP:Ce

1. INTRODUCTION

In recent studies of a number of scintillating materials it has been shown that scintillation parameters such as efficiency and speed can strongly depend on shallow charge traps [1, 2, 4]. The simple kinetic model based on existence of a number of electron traps and one recombination center (Ce^{3+}) allows for an easy explanation of temperature dependence of these parameters [1] and differences in scintillation properties between very similar materials ($YAlO_3$:Ce and $LuAlO_3$:Ce) [2].

In this contribution we will focus on the effects of shallow charge traps on emission kinetics of LuAP:Ce. We will show that temperature dependence of measured time profiles can be explained by a shallow trap interfering with the recombination process.

2. CRYSTALS AND EXPERIMENT

The investigated samples of LuAP:Ce were grown by means of the Czochralski technique by Litton Airtron. Although the Ce content in the melt varied from 0.25 to 2.00w%, in the material it is approximately 10 times smaller.

The measurements of time profiles were performed at the SUPERLUMI station of HASYLAB [3]. The sample was excited with the pulsed synchrotron radiation of the 236 nm and 78 nm wavelengths. The resulting Ce^{3+} emission was analyzed at the 360 nm wavelength. The instrumental time response of the set-up is below 1 ns.

3. THEORY

Recently it has been shown that the recombination process of free charge carriers created by high energy excitation can take two different routes [1, 2]. The first route is the direct one, when the carriers recombine at the Ce^{3+} ion 'immediately' (in time shorter than the time resolution of the set-up, < 1 ns). In this case the time evolution of Ce^{3+} emission does not differ from that of directly excited Ce^{3+} ion. Thus the time profile of emission ideally follows a single exponential decay with the time constant equal to radiative lifetime of excited Ce^{3+} ion - τ_{Ce} (usually due to set-up, there also is detectable rise of a signal described by a time constant τ_n). The second route, so called delayed one, as it has been shown, involves charge traps. In that case, although the emission originates from Ce^{3+} ions as well, its time evolution follows a different pattern and depends on the mean lifetime of the involved traps (τ_{trap}). In the simplest case of one trap the time profile can be described by the following formula:

* JG: E-mail: jglodo@phys.uni.torun.pl; AJW: E-mail: andywojt@phys.uni.torun.pl; Fax: 48-56-6225397;

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$$I(t) = I_0\left\{\frac{a}{\tau_{Ce}-\tau_n}\left[\exp\left(-\frac{t}{\tau_{Ce}}\right)-\exp\left(-\frac{t}{\tau_n}\right)\right]+\right. \tag{1a}$$

$$\left.\frac{b}{\tau_{Ce}-\tau_{trap}}\left[\exp\left(-\frac{t}{\tau_{Ce}}\right)-\exp\left(-\frac{t}{\tau_{trap}}\right)\right]\right\}, \tag{1b}$$

where τ_n is rise time of direct component ($\tau_n << \tau_{Ce}$), I_0 the total measured light, a and b branching coefficients. The first term (1a) corresponds to the direct component, whereas the second term (1b) describes the delayed component. The ratio of these two sorts of components is specified by the branching coefficients a (direct) and b (delayed).

It is important to note that in equation 1b the rise time will be equal to the shorter of the two time constants (τ_{trap} , τ_{Ce}) while the decay time to the longer one. Since the τ_{trap} varies with temperature therefore it is the key parameter in equation (1). Moreover τ_{trap} is a function of trap parameters (the activation energy E and frequency factor s):

$$\tau_{trap} = \left[s\exp\left(-\frac{E}{kT}\right)\right]^{-1}, \tag{2}$$

where k is the Boltzmann constant. This relation shows that by changing the temperature of the sample and studying the consequent variations of the time profile shapes (characterized in terms of decay and rise constants) it is possible to estimate the values of E and s. It can be easily seen if the equation (2) is rewritten in the following form:

$$\ln\left(\tau_{trap}\right) = \frac{E}{k}\frac{1}{T} - \ln(s), \tag{3}$$

that is equivalent to the linear equation of $y = \alpha x + \beta$. Using the equation (3) we can plot $ln(\tau_{trap})$ vs. T^{-1} and easily solve for the energy depth E and frequency factor s.

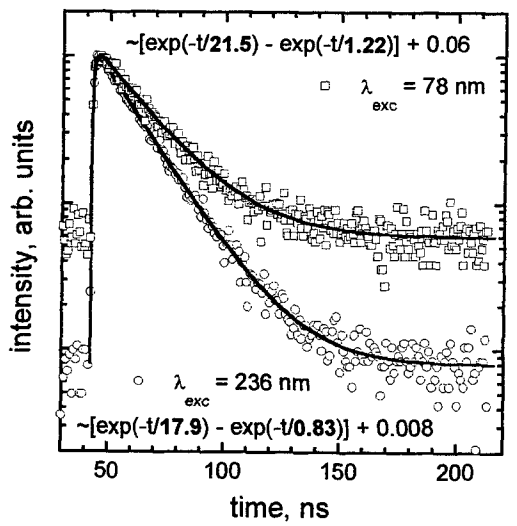

Fig. 1. Time profiles of LuAP:Ce 360 nm emission at 298 K. The experimental points measured under 78 and 236 nm excitation wavelength are shown by squares and dots, respectively. Note the differences in the backgrounds and time constants of two profiles. The solid lines represent fits to the points.

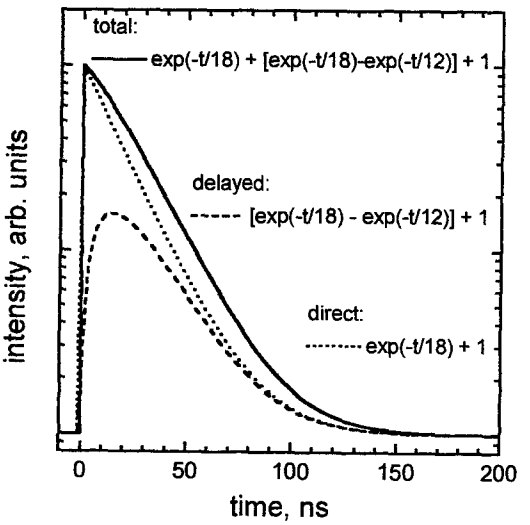

Fig. 2. Theoretical time profile calculated from the one-trap model. The dotted and dashed lines represent respectively the direct and delayed components. The solid line shows the sum of total. The delayed component modifies the profile as observed in experiment, see Fig. 1.

4. RESULTS AND DISCUSSION

In figure 1 we show two time profiles (TP) measured under 236 nm (dots) and 78 nm (squares) excitation at 298 K. The 236 nm light excites the Ce^{3+} ions directly (*4f-5d* transition) whereas the 78 nm light first more likely creates free charge carriers that excite the Ce^{3+} ions in the process of recombination (78 nm ~ 15.9 eV > 8 eV the band gap of LuAP). As we can see in the figure the difference in the excitation results in different time profile shapes. The most visible change is in the background level which in the case of the 78 nm TP is much higher (~10 times). This can be easily explained by the presence in 78 nm TP of at least one component that decays with the long time constant (much longer than the time scale of the measurement, ~200 ns). Such components are usually related to deeper traps (afterglow).

But more peculiar difference is that the decay time constants derived from fits are not the same. (A function used to fit both TPs had the following form: $\sim[\exp(-t/\tau_D) - \exp(-t/\tau_R)]$, where τ_D and τ_R denote the decay and rise time constants respectively.) Emission measured under the 236 nm excitation decays at 17.9 ns time constant, while under the 78 nm excitation at 21.5 ns. There also is a difference in rise time constants, 0.83 ns and 1.22 ns respectively, although in the case of emission under 236 nm excitation this constant has no physical meaning as it is introduced by the experimental set-up. Similar decay and rise time constants have been reported by Dujardin *et al.* [5].

Since the observed emission comes from the same Ce^{3+} ions the difference of almost 20% in the τ_D value is at first hard to understand. Similar discrepancies have already been observed and explained in YAP:Ce [1] or BaF_2:Ce [4]. The authors showed that such a lengthening of decay time constant in case of high energy excitation (γ) is due to shallow traps and takes place when the mean lifetime of carriers in traps is on the order of radiative lifetime of an activator (at a given range of temperatures). Such an effect can be easily seen in figure 2 where curves calculated according to equation (1) are plotted. The dotted line represents the direct component (equation (1a), τ_{Ce} = 18 ns, τ_n = 0.7 ns, a = 75%), the dashed line the delayed component (equation (1b), τ_{trap} = 12 ns, b = 25%) and the solid line the total. Presence of the delayed component modifies the shape of the total curve in a way that in the first approximation it reminds a single exponential

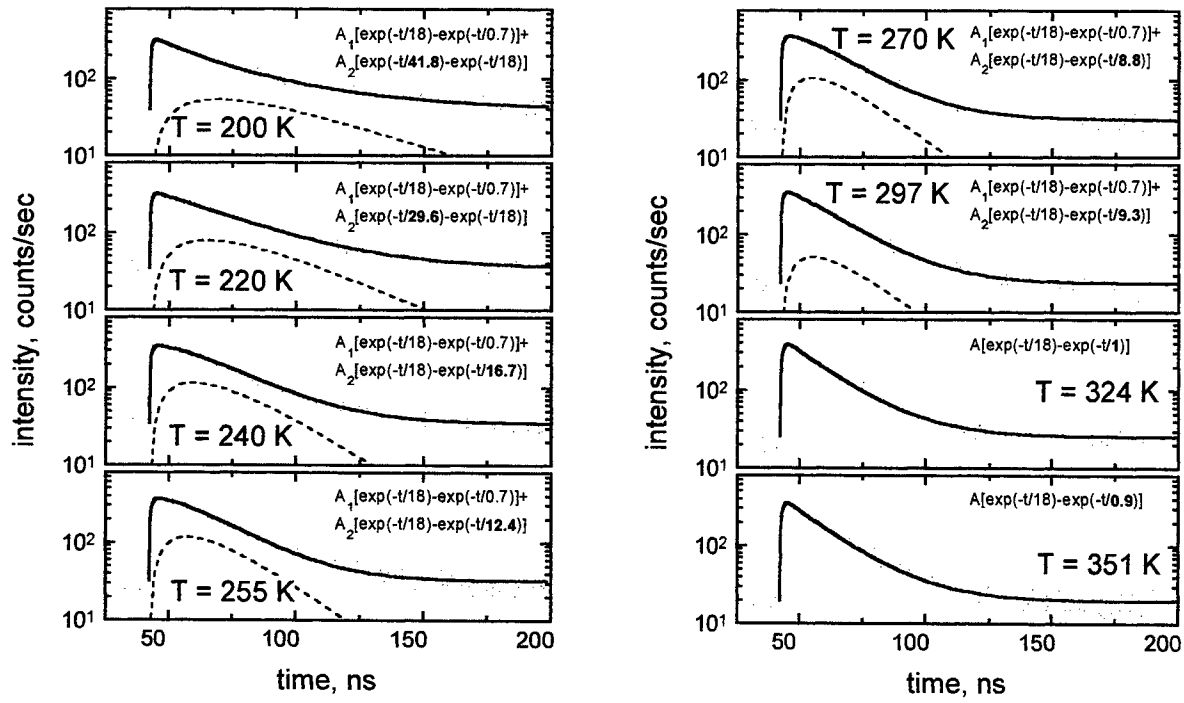

Fig. 3. Selected time profiles of LuAP:Ce 360 nm emission under the 78 nm excitation wavelength at different temperatures. Points are experimental data. The solid lines are fits calculated from equation (1) or in the case of 324 - 351 K traces equation (1b). The dashed lines represent the delayed component, see equation (1b). Note the changes in the delayed component with temperature.

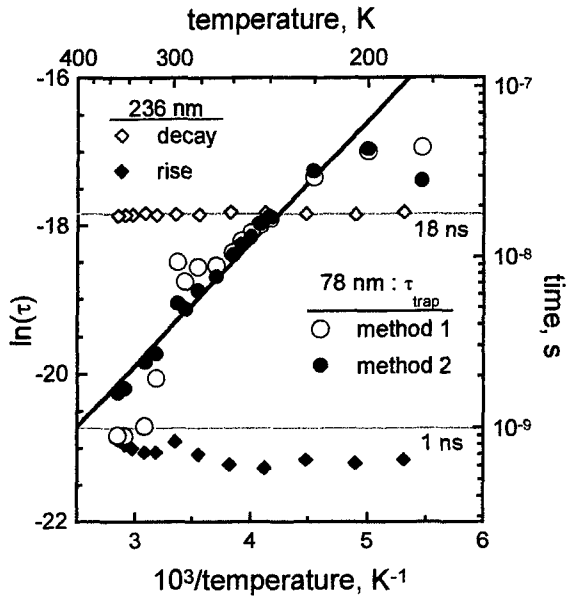

Fig. 4. Arrhenius type plot of decay and rise time constants derived from fits to the measured time profiles under 236 nm (diamonds) and 78 nm (dots) excitation. The solid line was calculated to parameters obtained from a fit (equation (3)) to the points (black dots). Acquired trap parameters are: E = 0.142 eV and s = 6.087×10^{10} s^{-1}.

decay. The time constant of such a decay is not equal to τ_{Ce} but is rather a function of both: τ_{Ce} and τ_{trap}, and in this case has the value of ~ 21 ns.

If the observed lengthening is indeed caused by a shallow trap the shape of the measured TPs should change with temperature as τ_{trap} does, see equation (2). In fact, conducted experiments show that TP shapes are temperature dependent. Examples of obtained traces are shown in figure 3 (points). Lines represent curves calculated with parameters extracted from fits to experimental points. In case of most traces a fitting function in the form of equation (1) was used (the sum of two components: direct and delayed). Additionally, as we assumed that the direct component is analogous to the emission of directly excited Ce^{3+} ion (at 236 nm) the time constants τ_{Ce} and τ_n were held fixed at 18 and 0.8 ns, respectively. Thus the only free fit parameters were: τ_{trap}, amplitudes I_0, a and b, and the background level. Only for the last three traces (324, 344, 353 K), as the τ_{trap} approached the value of τ_n and both components could be easily described as one, the fitting function in the form of equation (1b) was used. Obtained fit results are summarized in table 1 (method 1) and a plot of temperature changes of τ_{trap} is shown in figure 4 (open dots).

The fit results show that at lower temperatures τ_{trap} is relatively long (> 18 ns) and describes the decaying part of the delayed component (in figure 3 shown by dashed lines). As the temperature rises the τ_{trap} shortens and at 240 K the situation changes; τ_{trap} becomes shorter than 18 ns and from now on describes the rising part of the delayed component. If the obtained τ_{trap} values are put on an Arrhenius type plot, figure 4, it is easy to see that most of the points (open dots) lie along a line or at higher temperatures oscillate around this line. The alignment of these points can be improved if we

Table 1. Parameters derived from fits to emission time profiles of LuAP:Ce measured under 78 nm excitation. A fitting function was in the form of equation (1). Method 1: the τ_{Ce} and τ_n time constants were held fixed at 18 and 0.7 ns, respectively. Method 2: additionally the product $I_0 \times a$ was assumed constant. Negative values of b parameter indicate that τ_{trap} describes decaying part of the time profile instead of rising one, as it appears in equation (1). Note that τ_{trap} shortens with the rise of temperature.

	method 1				*method 2*				*method 1*				*method 2*		
T	bg	a	b	τ_{trap}	bg	b	τ_{trap}	T	bg	a	b	τ_{trap}	bg	b	τ_{trap}
K	-	%	%	*ns*	-	%	*ns*	K	-	%	%	*ns*	-	%	*ns*
183	50	66	-34	*43.9*	55.7	-34	*28.2*	270	30.6	61	39	*8.8*	31.3	43	*7.6*
200	39.5	57	-43	*41.8*	38.7	-44	*43.2*	282	28.4	66	34	*8.7*	29.7	40	*6.3*
220	35.0	53	-47	*29.6*	33.3	-49	*32.2*	291	27.0	71	29	*7.1*	28.0	36	*4.9*
240	34.3	50	50	*16.7*	34.0	48	*17.1*	297	23.6	77	23	*9.3*	24.9	30	*5.3*
245	33.7	51	49	*15.4*	33.5	48	*15.7*	314	26.0	58	42	*1.94*	25.7	30	*2.7*
250	33.9	54	46	*13.8*	34.5	47	*13.1*	324	25.1	0	100	*1.02*	24.5	28	*2.4*
255	32.1	54	46	*12.4*	32.5	47	*11.8*	344	21.4	0	100	*0.89*	21.3	23	*1.7*
260	32.1	55	45	*10.6*	32.4	45	*10.2*	351	19.5	0	100	*0.90*	19.4	20	*1.6*

assume while fitting the measured traces that the intensity of direct component does not change with temperature (i.e. $I_0 \times a$ product constant). Time constants (table 1, method 2) acquired from such fits are shown in figure 4 by black dots.

Because the τ_{trap} values depend not only on temperature but also on the trap parameters E and s, it is possible to estimate these parameters from a fit to the points (black dots) shown in figure 4, see equation (3). In a result of such a fit (in figure 4 solid line) the following values were obtained: $E = 0.142$ eV and $s = 6.087 \times 10^{10}$ s^{-1}.

The expected maximum of a glow curve calculated to obtained parameters is located at 60 K. Although the experimental glow curve [6] measured in this range of temperatures does not exhibit any strong signal (the main glow peak is at 180 K) there are relatively small peaks at around 55 and 90 K. Moreover, a trap of similar depth ($E = 0.205$ eV) has already been deduced from the analysis of scintillation light yield [2].

5. CONCLUSIONS

The experimental results and interpretation presented in this contribution indicate that apparent deviation of the decay time constant of Ce^{3+} emission in LuAP:Ce under the 78 nm excitation from the radiative lifetime of Ce^{3+} ion is artificial and can be explained by a shallow trap interfering with the recombination process. The analysis of time profiles measured against the temperature shows that trap responsible for the observed features has the following parameters: $E = 0.142$ eV and $s = 6.087 \times 10^{10}$ s^{-1}.

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